

Electronic supplementary information (ESI) for:

Organic thin film photofaradaic pixels for on-demand electrochemistry in physiological conditions

Maciej Gryszel and Eric Daniel Głowacki*

Experimental Methods

Materials:

Dichloro[2.2]paracyclophane (Parylene-C precursor) was supplied by TiXX Coatings Ltd. *N,N'*-dimethyl perylene tetracarboxylicbisimide - PTCDI (from BASF), Metal-Free Phthalocyanine - H₂Pc (from TCI) were both purified by ×3 temperature-gradient sublimation before use. All other chemicals, including gold (99.999%, beads 1-6 mm) were obtained from Sigma-Aldrich and used without any purification. The artificial cerebrospinal fluid (aCSF) solution ([Na⁺] = 153 mM, [K⁺] = 2.2 mM, [Cl⁻] = 135.4 mM, [H₂PO₄⁻] = 1.2 mM, [HCO₃⁻] = 26 mM, [Ca²⁺] = 2.4 mM, [Mg²⁺] = 1.3 mM, [glucose] = 10 mM) was prepared by dissolution in DI water of the following compounds: NaCl, KCl, Na₂CO₃, NaH₂PO₄ × H₂O, CaCl₂ × 2H₂O, CaCl₂, glucose; pH was adjusted to 7.4 with 1M HCl.

Fabrication of devices

Thickness control of the vacuum-deposited layers:

Thickness of all layers were controlled by quartz crystal monitors during evaporation/sputtering processes with tooling factors values determined with a Dektak 3ST profilometer beforehand.

Preparation of conducting substrates:

For fabrication of the PN-based photocatalytic systems, we prepared gold-covered (10 nm, by thermal evaporation) pieces of parylene-C foil (approx. 5 μm thickness). The fabrication process starts from chemical vapour deposition of parylene-C onto pre-cut pieces of PET foil (2 × 2 cm), using a CVD system provided by Diener electronic GmbH. For convenience of handling, the PET support of parylene-C was kept during all other preparation steps and experiments. Before gold deposition (by thermal evaporation at 3.0 Ås⁻¹ rate and at a base pressure < 2 × 10⁻⁶ torr), the surface of parylene-C was activated by O₂ plasma treatment (50 W, 120 s, Diener electronic GmbH system). Devices based on sputtered gold have also been tested. For this purpose, O₂ plasma treated, parylene-C substrates were loaded into a Vaksis 3M

sputtering system. Before deposition the vacuum chamber was evacuated to a pressure lower than $< 1 \times 10^{-5}$ torr. A gold target (of 99.999% purity) and DC magnetron was used for sputtering at a 3 mtorr pressure of argon, the average deposition rate was 5.4 Å/s. The substrate was not heated and remained at room temperature.

Fabrication of PN devices with evaporated Au back contact:

The gold substrates were placed with appropriate shadow masking (15 × 15 mm, stainless steel of 75 μm thickness, with a 5 mm Ø opening) in a 2-source vacuum evaporation system (Moorfield). H₂Pc/PTCDI PN layers of 30/30 nm thickness were evaporated from resistively-heated ceramic crucibles, at a rate of 0.5-3 Å/s and at a base pressure $< 2 \times 10^{-6}$ torr.

Fabrication of PN devices with electrodeposited Au back contact:

In the first step, gold substrates were used for electrodeposition of gold (details can be found in the following *Gold electrodeposition* section in this supporting note). The electrochemical cell design allows covering of a circle of 1 cm² (Ø 11.1 mm), during this process. The central part of this area, a Ø 5 mm circle, was masked with self-adhesive foil to leave a semi-transparent area as a substrate for the PN photosystem. After removal of self-adhesive foil, the stainless-steel masking (the same like in the case of PN-Au evaporated devices) was applied onto the substrate, with 5 mm Ø opening aligned to the area not covered by electrodeposited gold. The PN was deposited exactly as described above. For multilayered devices (thicknesses collected in Table S1), Au was evaporated (at a rate of 3 Å s⁻¹ in all cases) onto the PN system, after transferring samples to a metal-designated thermal evaporation system.

Table S1. Thicknesses of layers in multi-layered devices

Sample structure	Thickness of corresponding layer [nm]
PN: H ₂ Pc/PTCDI	30/30
PN/Au: H ₂ Pc/PTCDI/Au	30/30/5
PN/Au/PTCDI: H ₂ Pc/PTCDI/Au/PTCDI	30/30/5/30
PN/Au/PN: H ₂ Pc/PTCDI/Au/H ₂ Pc/PTCDI	30/30/1/30/30

Gold electrodeposition:

For better reproducibility of cathodic electrodeposition, to avoid interferences from products of anodic oxidation, the process was always performed in an H-cell (Redox.me, MM PEC H-CELL), using water solutions of HAuCl₄ (5 mM, with 20 mM NaNO₃) or K[Au(CN)₂] (0.12 mM, in 0.05 M NaH₂PO₄/ Na₂HPO₄ buffer, pH = 7.4). Before each deposition, the cathodic compartment has been deoxygenated by argon purging. Apart from parylene-C/gold substrate

(used as a working electrode during the electrodeposition process), the setup was also equipped with a Pt coil as counter electrode, Ag/AgCl wire in 3 KCl as a reference electrode. Measurements were performed with an Ivium technologies *Vertex One* potentiostat. Different deposition conditions (chronoamperometric, chronopotentiometric, cyclic voltammetric) were checked for all precursors. When using H₂SO₄ solutions, samples prepared by CV were of poor quality, all of them ultimately were discarded. From the point of view of H₂O₂ photoevolution performance, the best gold was obtained by chronoamperometric deposition in 2-electrode setup at -2 V vs. the counter electrode, until the charge passed was 0.5 C/cm². The average thickness of the gold layer, measured with Dektak 3ST profilometer, was 173 ± 45 nm.

H₂O₂ evolution performance and characterization of devices:

H₂O₂ photoevolution:

All H₂O₂ photoevolution experiments were performed with the experimental setup shown in Fig S1a, which consist of a red source (11 mW/mm², 660 nm) and a water-vapour saturated compartment, comprising a polystyrene (PS) petri dish (Ø 55 mm) with a few ml of water. A PDMS ring (4 mm thick, external Ø 15 mm; internal Ø 7.5 mm) was applied onto every device before the experiment in a way so that the PN-based photosystem was in the central part the well, which was later filled with 150 µL of aCSF. The solution was not oxygenated before the experiment, but it was constantly in contact with air. For uniform irradiation, every time before the experiment the devices were precisely aligned over the LEDs operating at 10% of their power. Aliquots of the solution to measure H₂O₂ concentration were taken at the end of the experiment. All experiments were performed at least two times, the final results given in figures were averaged, the error bars provided are delimited by maximum and minimum values of H₂O₂ concentration.

Determination of hydrogen peroxide concentration:

The quantification of hydrogen peroxide produced over the course of the experiment was done spectrophotometrically by following the oxidation of 3,3',5,5'-Tetramethylbenzidine (TMB) in the presence of horseradish peroxidase (HRP) and citric acid-phosphate buffer solutions. Values of absorbance were measured at 653 nm using a Synergy H1 Microplate reader (BioTek® Instruments, Inc.) in 96-Well PS flat bottom plates. Depending on hydrogen peroxide concentration in the sample, aliquots of different volumes (2-50 µL) were taken and added to the corresponding volume of HRP/TMB/buffer solution, in every case giving 300 µL of the

solution. The obtained absorbance values were recalculated to concentration values basing on calibration curve formulas ($R^2 > 0.998$ in every case).

SEM imaging:

SEM images were taken with SEM Zeiss Sigma-500 at an acceleration voltage of 3-6 kV, using the in-lens secondary electron detector. For this purpose, uncovered areas of samples were contacted to the SEM stage using copper tape and placed in the microscope chamber. Before imaging, samples were washed with DI water and dried with stream of N_2 .

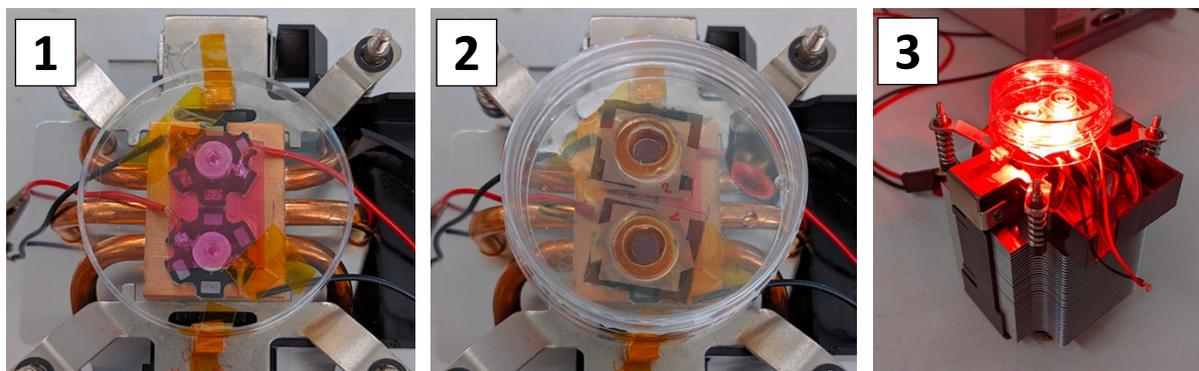
Measurements of electrical photoresponse (EPR):

The photovoltage generated by the devices was measured using setup and methodology presented in our previous work. Shortly, the potential difference under pulsed illumination (5 ms, 660 nm, 33 mW/cm²) was measured between the Au substrate and PN/electrolyte interface using PicoScope 5243B oscilloscope. Contact to the back electrode was established with a needle probe. The electrolyte contact was achieved with an Ag/AgCl wire placed in a syringe containing 0.1 M KCl electrolyte, precisely positioned above the sample in a way that only the solution was in contact with the PN structure, not the syringe itself.

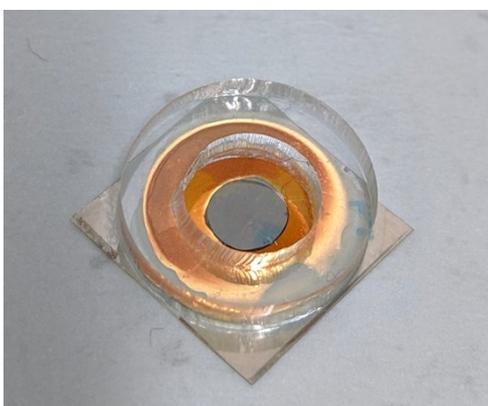
Electrochemical characterisation:

Characterization of the gold used for electrocatalytic oxidation of glucose was performed in a three-electrode system, with a gold sample as a working electrode, a Pt coil as counter electrode, and a Ag/AgCl wire in 3M KCl as a reference electrode, with an Ivium technologies Vertex One potentiostat. For the purpose of this experiment, gold was deposited over the entire 1 cm² area (Ø 11.1 mm circle) using the same conditions like for the actual PN device. To avoid possible interferences from trace amounts of the solution used for electrodeposition, samples were thoroughly washed with DI before the electrochemical measurement. All electrodes were placed in a Redox.me MM PEC 15 ml cell and deoxygenated before measurements by purging with argon. Active area of the sample mounted in the cell was limited by a proper o-ring to the size exactly of the electrodeposited gold area (1 cm², Ø 11.1 mm circle). The cyclic voltammetry experiments were performed with the 20 mV/s scan rate within 0.0 V to 0.4 V range. With more positive bias, values of registered current are much lower in a consecutive cycle. The same effect is observed when the scan rate is too low.

a)



b)



c)

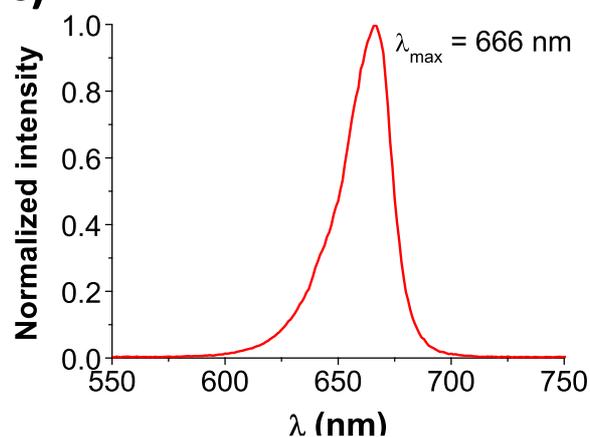


Fig S1. (a) Photographs of the photochemical setup used in this study, which consists of 2 x 3W red LED (660 nm) supported on a copper radiator and optical filter (100 nm of evaporated quinacridone pigment, to absorb all light of $\lambda < 600 \text{ nm}$), like in picture 1. Samples are placed in a polystyrene petri dish, saturated with water vapor to suppress water evaporation from the electrolyte during irradiation, like in picture 2. The beam of incident light is of 11 mW/mm^2 power. Picture 3 presents an ongoing experiment. The entire setup is cooled with a fan (placed 10 cm above, not shown for clarity). (b) Sample photo of the device based on electrodeposited Au (with PDMS well mounted) used for H₂O₂ photoevolution with red light. (c) Optical spectrum of the red light source used in all experiments.

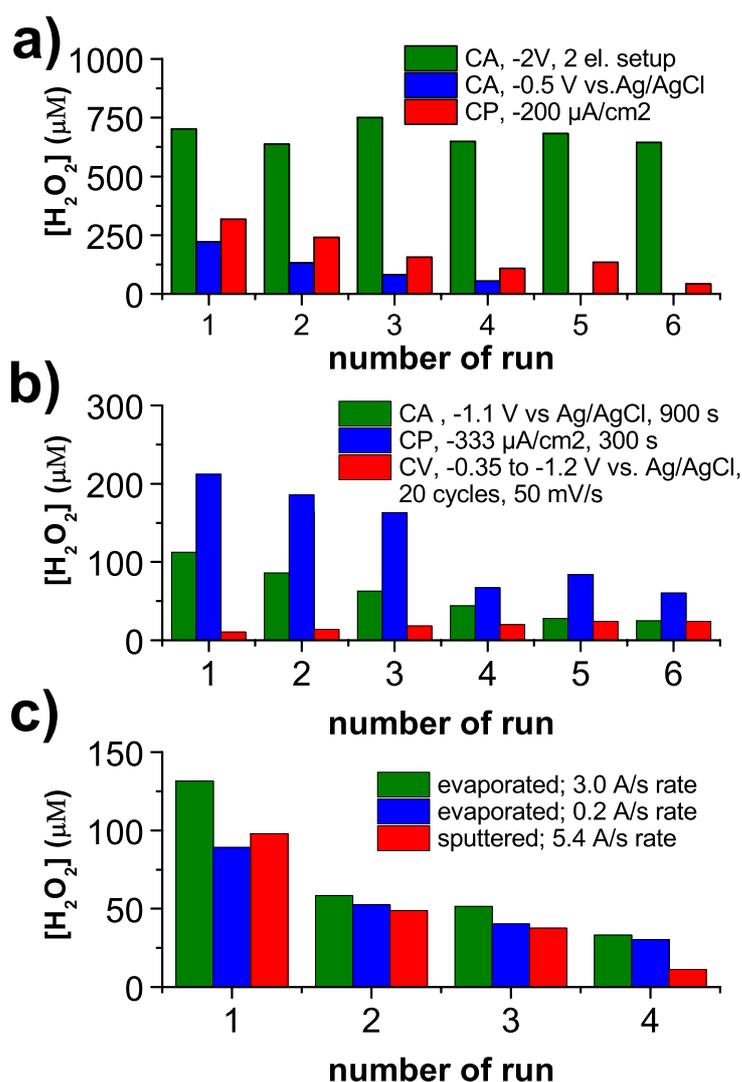


Fig S2. Comparison of H_2O_2 photoevolution performance of different gold anodes. (a) PN with electrodeposited Au using HAuCl_4 as the gold precursor. Gold from chronoamperometric deposition (CA) at -2V vs. counter electrode in 2-electrode setup performs better than from deposition at -0.5 V vs. Ag/AgCl in 3 electrode setup, although current density was very similar for both cases (approx. $500 \mu\text{A}/\text{cm}^2$). When chronopotentiometric (CP) deposition has been performed at this current density, the gold layer has a smooth structure of low performance, therefore for CP deposition with this precursor we used lower current density. (b) PN with electrodeposited Au using $\text{K}[\text{Au}(\text{CN})_2]$ as gold precursor. Different CA, CP and CV deposition conditions have been tried, the figure presents the best conditions for a given electrodeposition technique. (c) PN with vacuum-deposited gold. In the case of samples obtained by sputtering and thermal evaporation at a $3.0 \text{ \AA}/\text{s}$ rate, the electrolyte-exposed, catalytic gold is the same, continuous layer (10 nm) which lies underneath the PN structure, as shown in the Fig 1a. In the case of gold obtained by slow thermal evaporation at $0.2 \text{ \AA}/\text{s}$ rate,

due to its poor lateral conductivity which prevents from using it as a back contact, the device is based on the 10 nm gold by thermal evaporation at 3.0 Å/s rate, serving as a back contact and additional, 10 nm gold by thermal evaporation at 0.2 Å/s around the PN structure, serving as an electrocatalyst for glucose oxidation, like in the structures shown in ESI Fig S3.

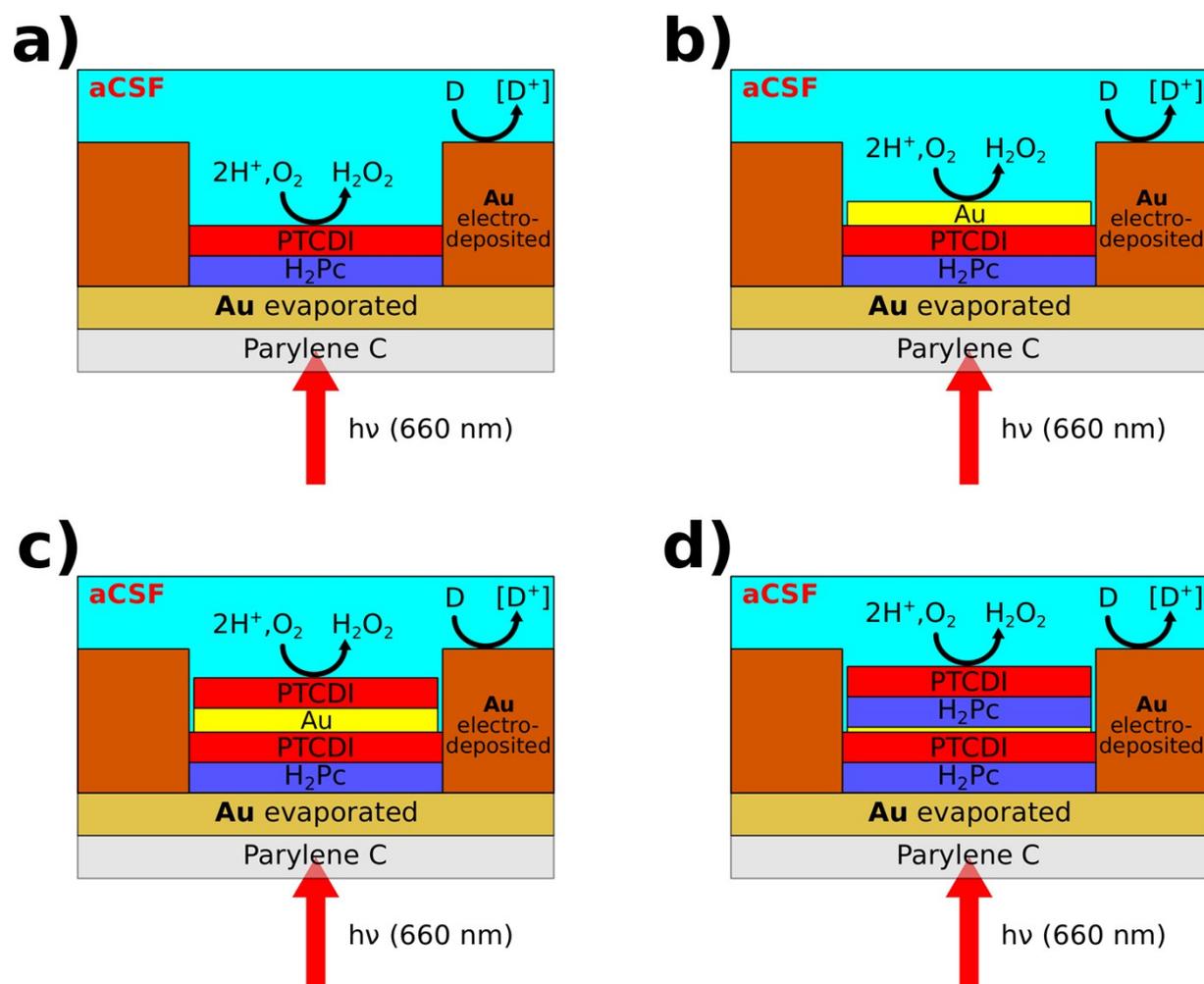


Fig S3. Schematics of different photochemical systems, based on organic PN junction and -2V electrodeposited Au: (a) PN, (b) PN/Au - compared with the simple PN structure, it has additional, 5 nm gold on the PN, deposited by thermal evaporation (3.0 Å/s). Diameter of the layer, 4.5 mm, is smaller than the PNs (5 mm) to prevent from shorting with the electrodeposited gold. (c) PN/Au/PTCDI, which is of the PN/Au structure, with additional, 30 nm of PTCDI. (d) PN/Au/PN, which is of the PN/Au structure, with additional PN, 30/30 nm. For better transparency, the thickness of the Au layer between PN junctions is reduced to 1 nm.

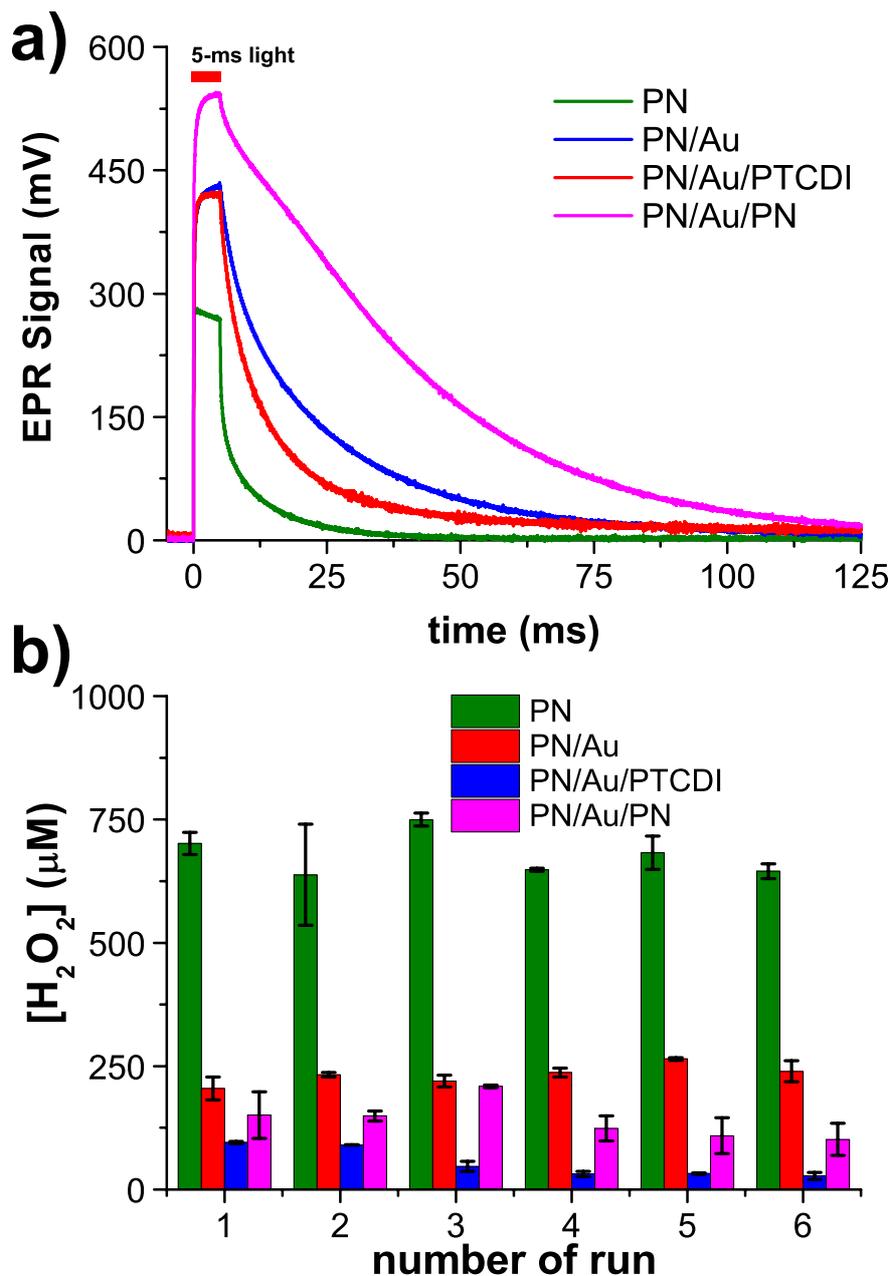


Fig. S4. a) Electrical photoresponse of the PN-based photofaradaic devices. Photovoltage of the PN system can be significantly increased by proper device design. The presented results are for fresh samples. b) H₂O₂ photoevolution with different photochemical systems, based on organic PN junction and electrodeposited Au. The chart presents the final concentration of H₂O₂ at the end of each, 30 min, experiment. In all cases, the performance is lower than in the case of simple PN structure. Schematic of all photochemical systems can be found in the supporting note, Fig S3.